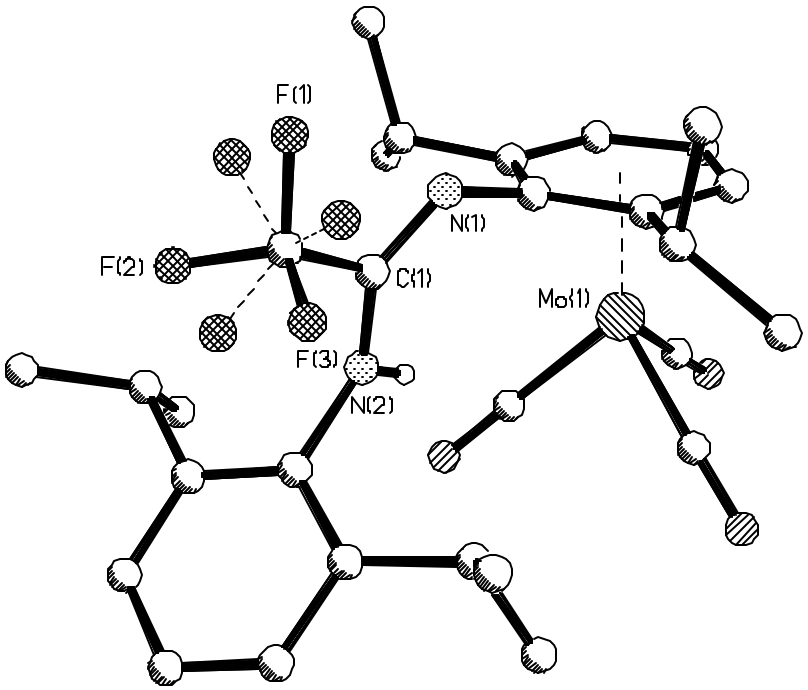
The University of Lethbridge

CHEMISTRY 3820 LABORATORY MANUAL

CHEMISTRY OF THE TRANSITION ELEMENTS



Ó **Anno Domini 2000**

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Chem 3820 Standard Periodic Table

1												13	14	15	16	17	18
1.0079 **H** 1	2																4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	3	4	5	6	7	8	9	10	11	12	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(261) **Rf** 104	(262) **Db** 105	(263) **Sg** 106	(262) **Bh** 107	(265) **Hs** 108	(266) **Mt** 109	110	111							

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

Developed by Prof. R. T. Boeré (updated July, 2000)

Monday	Wednesday	Friday	Lab
	6/9	8/9	8/9 3hr spectroscopy lecture
11/9 Last add/drop day 12th	13/9	15/9 Assignment #1	15/9 Lab intro & check-in *(attendance compulsory)*
18/9	20/9	22/9	22/9 LS1a
25/9	27/9 **Test #1**	29/9 Assignment #2	29/9 LS1b
2/10	4/10	6/10	6/10 LS2a
9/10 ***holiday***	11/10 **Test #2**	13/10 Assignment #3	13/10 LS2b
16/10	18/10	20/10	20/10 LS3a
23/10	25/11 **Test #3**	27/10 Assignment #4	27/10 LS3b
30/10	1/11	3/11	3/11 LS4a
6/11	8/11 **Test #4**	10/11 Assignment #5	10/11 LS4b
13/11 ***holiday***	15/11	17/11	17/11 LS5a
20/11	22/11 **Test #5**	24/11 Assignment #6	24/11 LS5b
27/11	29/11	1/12	1/12 Lab cleanup & checkout
4/12	6/12 **Test #6** *Last day of class*		

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Laboratory operation and evaluation

Assignment

(a) Students who do not have credit for 3810: Complete a total of 5 experiments as follows:
One experiment from each of Parts I, II, III and IV
The glassblowing course
(b) Students who have credit for 3810: Complete a total of 5 experiments as follows:
One experiment from each of Parts I, II, III and IV
One additional experiment from Parts I, II, III or IV

Students will work **in assigned pairs**, but must submit independent reports. ***Any evidence of passing-on portions of reports, either between partners, or to others, will be treated as plagiarism and prosecuted according to the rules of the University***. Shared work in the pre-lab exercises is, however, permitted (though not required). Beyond this proviso, the utmost cooperation and collegiality in the laboratory portion of this course is encouraged.

Glassblowing

Mr. Luis Delgado will instruct two sessions in glassblowing for each student (in small groups). These will be scheduled in laboratory periods. Each student must submit for evaluation to your instructor one example of each of the five projects assigned. A mark will be awarded, of equal weight with one "laboratory report and results".

Experiments

The lab is worth 30% of the total grade for Chem 3820. These 30 pts are broken down as follows (except for glassblowing and project labs):

Pre-lab exercises	5 pts
Laboratory reports and results	15 pts
Laboratory notebook	5 pts
Instructor's evaluation	5 pts
	30 pts

Each experiment carries equal value towards the total.

> *The pre-lab exercise must be completed in writing in the laboratory notebook at the start of each Experiment record, AND be discussed orally with the instructor no later than the morning before the laboratory period. A student who has not done so will be barred from the lab during that afternoon.*

The instructor's evaluation will be based on an assessment of the student's advance preparation and understanding of the experiment, industry, laboratory technique, safety consciousness, consideration of

others, cleanliness and tidiness, and the quality of the results. A sample of each compound synthesized must be available for examination by the instructor.

Laboratory Notebook

A complete accurate record is an essential part of chemical research. Although your Chemistry 3820 notebook is not a record of original research, an important objective of this laboratory is to provide some training in keeping a research notebook. The record of any experiment should be sufficiently clear that another chemist reading it could understand exactly what was done, what results were obtained, and if necessary repeat the work exactly as it was done. Your notebook will be judged primarily on how well it meets these criteria. Clarity and completeness are more important than neatness. It is not necessary to adhere to any particular format or organization.

A bound, hard cover, lined notebook is required. Spiral or loose-leaf notebooks are unacceptable. The pages should be numbered consecutively and some blank pages left at the beginning for a table of contents. Begin each experiment on a new page. If you have read the entire procedure in advance you will have some idea how much information is to be recorded. Leave enough space to record the experiment on consecutive pages. Each experiment should be dated. When the experiment extends over more than one laboratory period, a date should be entered at the beginning of the entries for each separate day's work or observations. (See Figure I-1.)

Include a short tabulation of the physical and chemical data of the compounds you are using, i.e. bp, mp, solubility etc. (consult the CRC Handbook for this information). Important equations (e.g. those developed for the pre-labs) should be included as well. All data are to be recorded directly into the laboratory notebook at the time they are obtained. Do not write data on a loose piece of paper for later copying. Nothing should ever be erased or removed from the notebook. If you make an incorrect entry, draw a line through the mistake and add a correction.

The laboratory notebook is also a good place to write down your thoughts and speculations as to the progress of your experiments. You may wish to include alternate methods and techniques in order to better achieve the end result. Finally include any notes that may aid you in understanding and writing up the experiment, e.g. structures, references, equations.

Laboratory Reports

You will be required to provide a short **typed** report on every experiment you perform. These reports should not be a regurgitation of the information provided in the laboratory manual, but rather a concise summary of the results obtained. Two or three pages will usually be sufficient.

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September 20th 1990

Preparation of potassium trioxolatochromate(III)

$K_2Cr_2O_7$ + $C_2O_4H_2$ + $K_2C_2O_4 \cdot H_2O$
294.19 90.04 184.24
$\longrightarrow$ $K_4[Cr(C_2O_4)_3]$ + CO_2

9.01 g of oxallic acid (100 mmol) is dissolved in 20 mL of d. H_2O, warming to 50°C

2.02 g of potassium dichromate (6.87 mmol) is added as a solid to the above solution in portions; vigorous effervescence occurs.

As the orange crystals of $K_2Cr_2O_7$ are added to the oxallic acid solution an instantaneous reaction occurs, leaving a very dark brown or black solution

After boiling this solution for about 2 min, 3.50 g (19.0 mmol) of potassium oxalate is added as a solid, rapidly. The solution soon turns a deep blue colour

After cooling the solution to R.T.

Figure I-1 Sample of notebook page

A statement of all experimental measurements should be provided. Specify the number of moles of reactants, reaction conditions and a simple sketch of the apparatus would be useful, as well as a description of any variations in the procedure from that outlined in the manual. Yields of products, melting points, spectral results and their interpretation should all be clearly and neatly laid out. References to background information, mechanisms, spectral or structural interpretation or any physical data, etc. should be included. The references should be listed under a separate heading at the end of the report, in the order in which they were cited. The format for such references varies from journal to journal; the style of Can. J. Chem. or Inorg. Chem. is recommended.

A crucial part of your write-up is your response to the points raised at the end of each experiment. These questions are designed to probe your understanding of the chemistry involved; you may well have to consult the literature cited in the manual in order to find an answer. One or more questions on the final exam will probably be lifted from the material covered in the laboratory, so you are advised to study these points carefully.

Each report will be due a week after the completion of the experiment. They must be handed in to your instructor, who will mark them. For "security" reasons the reports will not be returned to you until the last week of classes. Your grades, however, will be available one week after submission of the reports. Your lab note-books will be examined periodically during the lab periods and at the end of the semester.

Suggestions

Your instructor appreciates feed-back and constructive criticism regarding the operation of the laboratory and the design and effectiveness of the experiments. Suggestions are welcome.

"The boss sort of keeps an open mind."

General Laboratory Procedures

Use of Time

The efficient use of time is an asset not only to a student but especially to a researcher. Plan your experiments so that you will profitably use time which would otherwise be spent watching, e.g. a distillation, a sublimation or a non-hazardous reaction that need not be attended. This course allows some latitude in the planning of experiments and you should be constantly looking for opportunities to use the available time effectively.

Cleanliness

.....is next to Godliness. Since most of the experiments will involve the use of equipment which other students will use during the course, it is absolutely essential that all equipment be left in good condition at the end of each period. Any equipment which is broken should be reported to the instructor immediately so that a replacement may be found in time for the next class. Wash bottles of detergent, alcohol and acetone are provided at each sink, as well as scrubbers, sponges and rubber gloves. If you have difficulty cleaning a particularly dirty piece of glassware, notify the lab supervisor.

Balances and weighing

A great many experiments in chemistry involve weighing at some stage. Much time can be wasted over weighing procedures, and one of the biggest time wasters is the habit of weighing to a degree of accuracy in excess of the requirements of the experiment.

For synthetic work, including parts of most of the experiments in this course, weighing to 0.1 g or 0.01g is quite sufficient. Only for analytical work, such as in the characterization of some of the compounds prepared in this course, is greater accuracy required, on the order of 0.001 g or 0.0001g.

Even if weighing is only carried out to the required degree of accuracy, time can be wasted in the actual process, and unless some method is used whereby weighing is carried out rapidly, many experiments cannot be done in the time normally available.

At no time are chemicals to be weighed out onto to the pans of the ANALYTICAL BALANCES. These include **all the balances located in the balance room** (D-778), some of which are piezoelectric and some opto-mechanical. *All of these balances will be irreparably damaged by exposure to the kinds of chemicals you will be handling in this laboratory.* For synthetic work, you will use only the top-loading balances located in the lab (D-776). *Please do not disturb the Freshman classes by queuing up at the balances located in their labs.* Should you require a more accurate measurement than allowed by the top-loaders, follow the method of weighing by difference

described in the following paragraphs. *Although they are more robust, even the top-loading balances are susceptible to corrosion. Make it a practice to clean up any spilled chemicals on or around the balances immediately! Balances used in these laboratories (all types) cost between $2000 and $3000, and must be treated with respect.*

Suggested accurate weighing technique: weighing by difference

To weigh an accurate amount of solid (i.e. to the nearest 0.001 g or better) place a **weighing bottle** on a top-loading balance, tare it, and weigh out a rough amount of solid as close as possible to the accurate weight required. If the solid contains large crystals or lumps it should be lightly ground in a mortar before weighing.

The weighing bottle with contents is now capped, wiped clean and weighed using the correct procedure on the analytical balance, the weight being recorded immediately in your notebook.

Return to the lab, and tip the solid into your flask, vessel or whatever is suitable, no attempt being made to remove the traces of solid which will cling to the weighing bottle. *Return to the balance room*, and re-weigh the nearly empty bottle accurately. The loss in weight is the accurate weight of solid taken. This avoids the rather awkward process of washing out all the solid from the bottle and is quicker and more accurate.

The method is often used, as it is rarely necessary to weigh out an exact amount. It is bad practice to weigh out, for example, 1.25 g of a solid to make an exact 0.10 M solution. It is better to use the above method, finish up with a weight of 1.32 g and express the solution as

$$(1.32/12.6)\ M\ =\ 0.105\ M$$

This avoids the very messy practice of adding and removing odd crystals to try to get a weight exact.

By using the above method it is *never necessary* to have any loose chemicals near an accurate balance. The preliminary transfer is done at a rough balance, and only a closed bottle is used on the main balance.

Setting up apparatus

When ground-glass joints are used, it is not necessary to lubricate them except when high temperatures are involved. If a joint becomes seized, try the following methods of loosening it (a) rock the cone in the socket, (b) tape the joint gently with a block of wood, (c) warm the joint in a small flame, then tap gently, (d) soak the joint in penetrating oil, then try tapping.
A common cause of seizure is a caustic alkali. Try to keep alkalis off the ground-glass, and if they do get on it, wash thoroughly as soon as possible. Seizures can usually be avoided by dismantling the apparatus immediately after use. Where required, the procedures call for lubricating the joints with

silicone grease ("high vacuum grease"). *CAUTION: silicone grease may cause corneal damage. Make sure you wash thoroughly with soap and water to remove any silicone grease from your skin, to avoid accidental transfer of the grease to your eyes.*

Care should always be taken, when glass apparatus is set up, to avoid **strain**. It is best to start with one piece, and build up from there. To take the apparatus for distillation as an example

(a) Lightly clamp the flask at a height convenient for heating,
(b) Attach the still-head, screw-cap adapter and thermometer (no more clamps are needed for these),
(c) Attach the rubber tubing to the condenser, then position a clamp and stand so that the condenser will rest on the lower, fixed, side of the clamp. Attach the condenser to the still-head, and clamp lightly,
(d) Attach and support the receiver adapter and the receiver.

A similar procedure should be followed for the other assemblies.

Notes on individual assemblies

Reflux Clamp the flask and the condenser. If an air condenser is used, clamp it at the top.

Distillation Use a vented receiver adapter in the following circumstances:

(a) if a noxious gas or vapour is given off, and must be led off by rubber tubing to an absorption apparatus or a sink,
(b) if an inflammable vapour is given off (for example in ether distillation), and must be led off by rubber tubing to below bench level.

Where an air condenser is specified, it is frequently adequate to attach the receiver adapter directly to the still-head.

Fractional distillation Clamp the fractionating column only at the top. If a column is not available, a vertical air condenser or an ordinary condenser with an empty jacket can be used instead, though it will be less efficient.

Gas evolution A 250 mL flask, with a B24 joint, and a 100 mL dropping funnel are satisfactory for most purposes. If these are not available, it is convenient to prepare a number of standard rubber stoppers, each carrying a dropping funnel and a delivery tube, which will fit 250 mL wide-necked flasks.

Gas drying If ground-glass jointed apparatus is not available, a 250 mL conical flask with a rubber stopper is perfectly adequate.

Gas absorption If it is necessary to dissolve a gas in a liquid, the best method is to use a Büchner flask fitted with a wide glass tube in a rubber stopper. This overcomes the 'suck-back' problem by equalizing the internal pressure with that of the atmosphere.

Use of corks Even when apparatus with ground-glass joints is normally used, there are still occasions when corks are required. For efficiency corks must be rolled before use, and bored with care. A cork of the correct size should only just go into the neck of the flask. Soften it by rolling between the fingers, or between sheets of paper on the bench. Never try to roll a cork which already has a hole in it; it will almost certainly split.

To bore a cork, or a rubber stopper, choose a sharp borer slightly smaller than the tube or thermometer which is to go into the hole. Hold the cork in the hand, and push and rotate the borer until the hole is approximately half way through it. Now reverse the cork, and continue boring from the other end until the holes meet in the middle. Now use a rat-tailed file to increase the size of the hole until the tube or thermometer fits it with gentle pushing, but with no strain. Place the cork on the file, and rotate it with the hand or on the bench; do not use a sawing action as this will cause an eccentric hole which is likely to leak.

When inserting tubes or thermometers into holes in corks, it is an advantage to moisten them with a little ethanol as a temporary lubricant. If a cork becomes stuck to a tube or a thermometer during use, it is best to cut it off, rather than risk breakage. *The majority of cuts which occur in the laboratory happen when pushing tubes through, or removing them from, corks.*

Reflux and distillation

Unlike ionic reactions, which are frequently extremely rapid, reactions between covalent substances tend to be slow. Particularly in main-group and organometallic reactions, it may be necessary to keep a reaction mixture hot for a matter of hours. This, coupled with the fact that volatile and inflammable solvents have to be employed, makes it necessary for special equipment to be used.

Reflux The use of a reflux condenser is often necessary. It is used whenever a reaction mixture has to be kept boiling for an appreciable time and the solvent is volatile. A water condenser may be used for solvents boiling up to about 130 C, and for higher boiling-point solvents an air condenser is adequate. The flask must never be filled more than half way, the size of flask is chosen by consideration of the total volume of the reaction mixture. A piece of boiling stone or similar substance is used to promote even boiling for all reflux procedures, or else magnetic stirring is employed. The object of the apparatus is to keep the solution hot while the reaction is proceeding, without loss of solvent. It is pointless to boil violently, and the heating should be controlled so that the solution is merely simmering. The flask may be heated by an **electric**

heating mantle controlled by a Variac **(NEVER plug a heating mantle directly into the mains!)**, or by using an oil bath on an electric hot plate.

Distillation The purpose of distillation is to purify a liquid, or to remove a solvent from a solution. The flask must never be more than half full, boiling stone or magnetic stirring must always be used, and the choice of condenser is the same as for reflux work. The heating of the flask may be by any of the usual means. Distillation of a liquid to purify it should be at such a rate that no more than 2 drops per second of distillate are obtained. On the other hand, removing a large quantity of solvent may be done much more rapidly.

Fractional distillation The purpose of fractional distillation is to separate two liquids of different boiling-point. As with other forms of distillation, the flask must never be more than half full, and boiling stone or magnetic stirring must always be used. To get a good separation of the liquids, it is essential that the distillation be carried out very slowly. The slower the distillation the better the separation. A rate of 1 drop per second of distillate should be the aim.

Since the efficiency of the process depends on the fractionating column reaching thermal equilibrium (that is, there should be a gradual increase in temperature from the top to the bottom of the column), best results are obtained if drafts are excluded. The source of heat should be steady, and not intermittent.

Use of the separating funnel

The separating funnel is used for several important processes. Unless care is taken, its use can be one of the major causes of mechanical loss. The choice of size is particularly important and, as with flasks in distillation, the smallest which will do the job is best.

Separating two immiscible liquids

The liquid mixture is poured into the funnel, and the funnel is gently agitated to assist in the separation into layers. The funnel should always be stoppered, but if a particularly volatile substance, such as ether, is present, the funnel should be vented occasionally through the stopcock *(hold it slightly inverted while doing this)* to avoid the possible buildup of pressure.

When separation into layers has occurred, the stopper is removed and the lower layer run off into a small flask. Swirling the funnel and allowing separation to occur again frequently provides a further small sample of the lower layer.

The top layer is poured from the top of the funnel into a second flask. It is a wise precaution always to keep both liquids, even if one of them is to be discarded. It is surprising how often the wrong layer is thrown away!

Washing a crude liquid

One of the commonest procedures consists in shaking up a crude liquid product with an aqueous solution to remove some of the impurities present. The reagents should always be used in small quantities, and the process repeated if necessary. Mechanical loss is always greater when large volumes of washing solutions are used.

Gases are often formed in considerable quantities during the cleaning process, and it is essential to release the pressure frequently. This is best done by inverting the well-stoppered funnel and opening the tap.

If the required substance is the top layer, then running off the bottom layer is quite simple. The whole of the bottom layer of waste should not be run off each time. It is better to leave a little of the aqueous solution, and add further fresh reagent. The careful separation is only done when running off the last of the various washing solutions. This avoids the risk of inadvertently letting out of a few drops of the product being treated.

When the required substance happens to be the bottom layer, avoiding mechanical loss becomes more difficult. If the product is run off between each wash and then returned to the funnel for the next, the loss becomes very great. The best compromise is obtained by using rather larger volumes of washing solutions, and decanting the spent solution from the top of the funnel. In this way the product never leaves the funnel until the final wash is over. It is then run out into its receiver, leaving the final washing solution in the funnel.

Liquid extractions

The separating funnel is often used to extract a solute from one solvent by means of a second solvent immiscible with the first. The removal of a solute from water by means of ether is one of the commonest applications.

The size of the funnel is chosen to accommodate the whole of the aqueous solution if possible. This saves a lot of time which would be spent in repetition. A series of extractions with a small quantity of ether is more effective than one with a large amount of ether. In practice the volume used is that which gives the smallest manageable top layer, bearing in mind that the ether solution must be decanted from the top of the funnel. If the layer is too small, decantation becomes difficult. The solution is usually extracted about three times with fresh quantities of ether, and all the ether extracts are decanted into one flask. After the final extraction the aqueous layer is run off, and the last ether layer decanted completely into the flask. The ether solution is then dried, and the ether removed by distillation to obtain the solute.

Filtration methods

There are a variety of techniques used for the separation of a liquid or solution from a solid.

Simple filtration

The use of a filter funnel and a piece of filter paper folded into four is usually reserved for ionic substances precipitated from aqueous solution. Precipitates obtained in qualitative analysis and inorganic problem work are often rather fine, and cannot be efficiently filtered at the pump. But covalent solids are usually to be separated from a volatile solvent, and the comparative slowness of simple filtration brings in complications caused by evaporation.

It is essential in simple filtration to ensure that the paper is really carefully folded. The paper must be fitted carefully into the funnel and wetted thoroughly with water, or the appropriate solvent, before filtration is started.

The contents of the filter paper should not reach within half an inch of the top of the paper. These simple precautions can make all the difference to the time taken for a filtration to reach completion, and should never be neglected.

Filtering of organic liquids

This is usually done to remove solid impurities which are not in a very fine state of subdivision. A normally folded filter paper will do for this, but the 'fluted' filter paper gives a faster rate of filtration. Basically a fluted filter paper is one that is folded to give a corrugated effect which allows the whole of the paper to be active rather than half as is the case with simple filtration.

There are a variety of ways of folding such a paper; one of the easiest is as follows.

> The paper is carefully folded in half, opened out, and then folded in the same direction at right angles to the original fold. The paper is then folded twice more, the folds being all in the same direction and mutually at 45°. Each section is now individually folded in the opposite direction. The result is a fluted paper with sixteen faces. This is placed in a suitable sized funnel, and pushed down so that the ridges all touch the side of the funnel. Since all the paper is being used, only one layer thick, filtration is appreciably faster.

For filtering a small amount of liquid to free it from a drying agent it is better to use a very small piece of cotton-wool, pushed lightly into the top of the funnel stem, or even into the narrow part of a disposable pipette. The mechanical loss entailed by absorption on a filter paper is thus obviated, and much higher yields of product obtained.

The Büchner funnel and filter pump

This system of filtration is the most widely used when dealing with recrystallized substances. The Büchner funnel may be attached to the flask by means of a cork, but a much more useful device consists of a flat piece of rubber with a hole in the center capable of receiving the funnel stem and making a good seal.

The disc of rubber allows, within reason, any size funnel to be fitted to any size flask. If this method is adopted, then the size of the funnel chosen is the smallest that will hold the solid, and the flask is similarly chosen to be the smallest that will hold the liquid, if both solid and liquid are required. If the solid is to be discarded, than a large funnel can be used to increase the rate of filtration. If the liquid is to be discarded, then the flask may be large enough to take all the liquid as well as the washings.

This choice of size is important, as mechanical loss can be very great during filtration.

The filter-paper disc is placed in the funnel, and wetted with the solvent present in the solution to be filtered. It is essential that the funnel and flask be perfectly dry. If the solvent concerned is ethanol, then the paper may be wetted with water. The pump is turned on and the paper pressed into place. During filtration the pump must never be turned off, as this may cause water from the pump to be drawn back into the filtrate. When all the material has been filtered, the pump is disconnected from the flask while the pump is still running. If some of the solid has not been transferred to the funnel, a portion of filtrate is retrieved and used for swilling the residue into the funnel. The solid is washed free of filtrate by pouring a small portion of chilled fresh solvent into the funnel while the pump is disconnected. Finally, the solid is drained as dry as possible by suction from the pump and pressure from a clean glass stopper.

Gravimetric filtration

In quantitative work it is essential that all the solid be transferred, and retained in the filter funnel. A **filtering crucible** with a porous sintered-glass bottom is the most convenient apparatus to use. Porosities from 0 (coarse) to 5 (very fine) are available, although for most purposes porosity 3 is best; a few fine precipitates will require porosity 4.

The sintered-glass crucible is dried in an oven, cooled, and accurately weighed before use.
To collect the solid the pre-weighed crucible is set in the mouth of the Büchner flask by means of a firm rubber cone. The pump is turned on, and as much supernatant liquid as possible is decanted off through the crucible. The liquid should be directed into the crucible down a glass rod.

The solid is then transferred, using a gentle jet of water to swill out all particles. If solid clings to the apparatus, it can be rubbed off using a glass rod protected with a **rubber 'policeman'**. The pump

suction at this stage should be as gentle as possible, otherwise the porous glass may clog. Finally, the solid and crucible are washed repeatedly to remove all soluble materials, and dried to constant weight.

Drying methods

The drying of liquids

In the majority of cases with organic liquids extreme drying is not usually necessary, and drying agents like *anhydrous calcium chloride* or *anhydrous sodium sulfate* are adequate. Of the two, calcium chloride is the more efficient, but also the more messy.

As calcium chloride will remove water and ethanol, it is employed when both need removing but, if the drying is only to remove water, anhydrous sodium sulfate is generally employed. Sodium sulfate will only work at temperatures below 30°C and should be used at room temperature. It is capable of removing its own weight of water, and the use of too much drying agent should be avoided at all times. The drying agent will be 'wetted' with the required product, and a large mechanical loss will be entailed.

In order to dry an organic liquid, whether a product or a solution containing the product, it is placed in a suitable sized conical flask, fitted with a good stopper or cork, and the drying agent added. The corked flask is shaken at intervals, and left for at least five minutes, preferably longer.

If sufficient drying agent has been used some should remain unchanged in appearance: i.e. an opaque powder of sodium sulfate or firm granules of calcium chloride.

The drying of solids

There are various methods of drying solid materials. When deciding which method to use it is important to know something of the physical properties of the material. If dehydration of a hydrate or melting of an organic solid occurs, recrystallization has to be repeated with further loss of time and material.
Although the method of air drying takes longer than the others, it is one of the safest for non deliquescent solids. The damp solid, drained as dry as possible on the filter, is transferred to a watch-glass and spread out evenly. This can be left to dry overnight in some dust-free place. If possible a second, larger watch-glass should be arranged over the product as a precaution against dust, but this cover should allow free evaporation.

Though the desiccator is ideal for many solids, care must be taken when drying hydrates. It is quite possible to lose some water of crystallization if the dehydrating agent is very effective.

Samples to be dried should be spread out on a watch-glass and labeled with their name and date.

The desiccator must be regularly recharged with fresh desiccant, and the ground-glass seal kept greased with the minimum of silicone grease, so it appears transparent. A few desiccants are listed in Table I-1 with comments on their relative usefulness.

Table I-1 Common drying agents

Desiccant	Remarks
Phosphorus (V) oxide	Expensive, fast and efficient
Concentrated sulfuric acid	Cheap, hazardous, fast and efficient. If $BaSO_4$ is dissolved in the acid, it precipitates when the drying capacity is exhausted.
$CaCl_2$	Cheap, moderate effectiveness. Use if ethanol was the solvent
Soda-lime	Use if acidic vapours need to be absorbed.
Silica gel	Readily regenerated, limited effectiveness. Changes colour when exhausted if stained with $CoCl_2$
Drierite	(Anhydrous sodium sulfate) Commonly stained with $CoCl_2$; Blue when fresh, red when exhausted. Very inert; use for most applications.
$MgSO_4$	Ensure it is anhydrous! Used to dry organic liquids, especially ethers.

It is important to remember that after opening a desiccator takes at least two hours to re-establish a dry atmosphere.

A vacuum desiccator is used to speed the drying of a sample. The sample must be covered with a second watch-glass and the desiccator evacuated and filled slowly to avoid blowing the sample about. A vacuum desiccator must be covered with strong adhesive tape, or be enclosed in a special cage, when being evacuated and de-evacuated to guard against an implosion.

Recrystallization and purification of solids

Inorganic solids, when first prepared, are rarely pure. The original solid must be recrystallized from an appropriate solvent. If the solvent is a flammable liquid, as it often is, it is better to carry out a recrystallization under reflux, until experience has been gained. With ethanol, a very common solvent, it is quicker and neater to use a conical flask, but this does entail a risk of fire.

Reflux method

The solid is placed in a suitable sized flask, preferably a conical flask as it can be easily put aside to cook, and a condenser attached. A little solvent is poured down the condenser and the mixture raised to boiling point. If all the solid has not dissolved, a little more solvent is added after removing from the hot plate, until the solid just dissolves at the boiling-point. If there are no insoluble solid impurities, the solution will be clear. It is removed from the hot plate, and slowly cooled to room temperature. Gentle swirling of the flask may be required to initialize crystallization after the solution reaches room temperature. The solid usually crystallizes on cooling, but, if slow to start, scratching the inside of the flask with a glass rod frequently helps crystals to form. The flask should be cooled at least to room temperature, or preferably rather lower by placing the flask in iced water or in a refrigerator.

The pure product is filtered off at the pump. It is essential for the filter flask and funnel to be clean and dry, except for the solvent concerned. The mixture to be filtered is poured on to the filter paper and the solid remaining in the flask is washed out with the filtrate. This is important. The filtrate is, of course, a saturated solution of the required solid, and so the filtrate cannot reduce the yield by dissolving some of the crystals. The filtrate is used for washing out the flask several times until all the solid has been transferred to the filter. On no account should fresh solvent be used for transferring the solid to the filter.

The recrystallized solid is then dried in a suitable manner, bottled and labeled.

Open flask method

This is essentially the same as the previous method, but is carried out directly on the hot plate with an open conical flask. The solvent is only just allowed to come to the boil and then the flask is removed. It is possible to see the vapour condensing inside the flask, and there should not be a risk of fire if care is taken. The obvious advantage of this method is its speed. The method is not suitable for low-boiling solvents such as ether.

Recrystallization requiring hot filtration

If, during a recrystallization, there is an insoluble solid impurity, it becomes necessary to filter the hot solution. Care must be taken that no crystallization occurs during the process as this would block up the filter funnel and cause great difficulty. To avoid this, the following procedure is used.

> The crude solid is dissolved in the solvent in the normal way, and when all the solute has just dissolved at the boiling-point, a further small quantity of solvent is added. This ensures that the solution is not saturated. This solution is kept hot while a separate sample of solvent is

heated to boiling and then poured through the prepared Büchner funnel. This procedure heats up the funnel and flask. The filter paper, which must be in position, is held in place by a glass rod. The funnel chosen should be reasonably large. Not only does this retain the heat better, but filtration will be faster.

The hot solution is now filtered rapidly with the pump full on. As soon as all the solution is through the funnel, the pump is disconnected and the funnel removed.

At this stage the solute will almost always have begun to crystallize out in the Büchner flask. To save mechanical loss, the solution should be kept in the Büchner flask and cooled in the normal way. The final filtration to collect the crystals therefore requires another Büchner flask.

The use of activated charcoal

Sometimes there are coloured impurities present in the crude material to be recrystallized. These are removed from the solution while hot by adsorption on activated charcoal.

The recrystallization is carried out normally until the crude material is dissolved. A little extra solvent is added, and the mixture cooled slightly. A small amount of activated charcoal is added to the cooled material. It is important to cool the solution before adding the charcoal, as this material tends to promote boiling. Often the whole solution will boil over violently on the addition of charcoal if insufficiently cooled.

The mixture with the charcoal is allowed to boil gently for a few minutes, and is then filtered hot, using the method described above. It is important to ensure that the paper is well fitted or charcoal may get round the edges and spoil the product. As in hot filtration, the funnel should be large so that the filtration is as rapid as possible. The flask should be of a suitable size for the volume of purified solution obtained.

Column chromatography

Chromatography using columns of adsorbent material is useful for separations on the preparative scale, because gram quantities of material are readily purified. Many adsorbents are available, but these experiments all use aluminum oxide or silica gel.

Packing the column

Clamp the glass tube upright and, checking that the tap is closed, half fill with the solvent required for the experiment. Push a pad of non-adsorbent cotton-wool or glass-wool to the bottom of the tube; do not ram it down hard.

Now slowly pour in roughly 25 g of chromatographic aluminum oxide or fine silica gel. Use a filter funnel to guide in the powder and, if a blockage occurs (e.g. just above the solvent level), rock the tube gently. Also tap the tube gently with your fingers to settle the powder uniformly and release any trapped air bubbles.

Push a second pad of cotton-wool down the tube to protect the upper surface of the column from disturbance. Drain off the excess solvent until the level falls to the upper cotton-wool pad; never let the solvent level fall lower, otherwise the uniformity of the column will be ruined by trapped air bubbles. The column is now ready for use.

Loading the column

Place a sample on the column using a pipette; a precise volume is not required, but the use of a pipette ensures that the sample is placed directly on top of the column and does not drain down the tube walls. Allow the column to drain slowly and wash in the sample by adding small portions of fresh solvent. The sample should now be adsorbed as a narrow band at the top of the column.

Developing the column

Develop the column by running solvent through. Fill up the tube with solvent, then allow solvent to pass through at the rate of about 5 mL per minute. Keep the tube topped up, as the liquid pressure will encourage a good flow rate and there will be less danger of letting the column run dry. If the flow rate is too slow, pressure can be applied by attaching a small hand bellows to the top of the tube.

Collect equivolume fractions of solvent draining from the column. Coloured materials are readily seen as they are eluted from the column, but colourless substances must be found by evaporating the fractions to dryness, or by running t.l.c. on each fraction.

Thin-layer chromatography

In thin-layer chromatography (t.l.c.) a suitable adsorbent is spread on a glass plate. After activation of the adsorbent by heat, the plate is spotted with a dilute solution of the material under study and then developed with a suitable solvent. When the solvent has risen a convenient distance up the thin film, the plate is dried and treated with a detecting agent. Commercial plates with plastic or foil backing are also available, and are extremely convenient for occasional use.

Silica gel is the preferred adsorbent for t.l.c., although cellulose and alumina thin films are readily prepared. In all cases the adsorbent must have been specially manufactured for t.l.c. work, and it is simpler to use materials free of special additives or binders. T.l.c. is faster than the other techniques in

general and sharper separations are possible, but to master the method you will have to work with care and ensure your apparatus is properly cleaned.

Preparing the plates

(a) A slurry of roughly 30% w/v of silica gel in chloroform is kept in a well-sealed wide-mouthed bottle, and microscope slides are coated by dipping them into the slurry.
The slurry bottle should be placed on a large sheet of blotting paper in a fume cupboard.
Shake the slurry bottle and then dip in two well-cleaned microscope slides, held together at the top by crucible tongs. Dip in and lift out the slides in a continuous movement; do not coat the top 1 cm of the slides. Allow to drain briefly. Handling the edges only, ease the slides apart and lay them, thin film uppermost, on the blotting paper for five minutes to dry.
Activation is not necessary.
If the film is not uniform, the microscope slide was not clean.

(b) Prepare a slurry of 1 g of cellulose in 5 mL of acetone by mixing well in a small glass mortar.
Hold a 15 cm x 5 cm glass plate over a sheet of blotting paper and pour the slurry on to one end of the plate. By gently rocking the place, spread the think film uniformly over the plate, then lay it down for five minutes to dry.
Activation is not necessary.
By use of the same technique it is possible to spread on 15 cm x 5 cm plates slurries of alumina or silica gel (1 g in 2.5 mL of 85% aqueous ethanol; if the slurry proves too thick or too thin, vary slightly the volume of solvent).
Allow to dry at room temperature, then activate in an oven at about 120°C for thirty minutes.

Spotting the plates

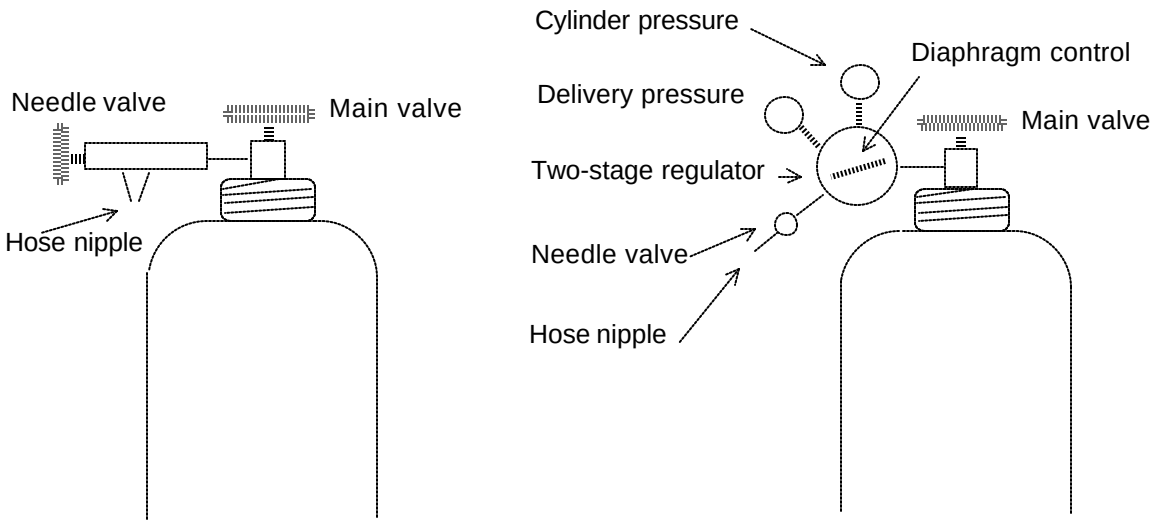
Thin films must be handled and spotted with extra care because of their fragile nature. Spot the plates with not more than 0.002 mL of 0.1-0.01 M solutions from a capillary or fine wire loop. If possible, solutions should be prepared in the same solvent that will be used for development of the chromatogram.

As many as three separate spots can be placed on a microscope slide, if channels are scratched in the thick film with the edge of a spatula and surplus material is cleaned from the edges of the slide.

Compressed Gas Cylinders

Several experiments make use of gases which are commercially available in compressed gas cylinders. They come in a variety of sizes with several valves and regulators. The metallic content of the values

may be dictated by corrosive properties of the gas. The facile reaction of N_2O_4 with copper, for example, requires that the cylinder and valve contain very little copper. Many cylinders contain a safety valve or nut which is designed to rupture if the pressure inside the cylinder exceeds the specifications of the cylinder. Under no circumstances should anyone tamper with the safety nut.



(a) Gas requiring only a needle valve

(b) Gas requiring a two-stage diaphragm regulator

Figure I-2 Detail of the two main types of compressed gas cylinders used in the lab

The main valve (Figure I-2) on a cylinder is simply an on-off valve which allows no control of the gas flow; it should always be used with some type of control valve. A needle valve permits such control but if the cylinder contains a compressed gas, the cylinder pressure will decrease as the cylinder is used and the gas flow will likewise decrease. Thus for compounds which exist as gases (e.g. CO, N_2, BF_3) in a cylinder, a given flow rate cannot be maintained without continuous adjustment. Compounds which condense to form liquids under pressure exert their natural vapour pressure so long as any liquid remains in the cylinder. For these gases (e.g. MeBr, NH_3) a continuous flow rate can be obtained with a needle valve.

To achieve a constant flow rate for gases which do not condense under the pressure in the cylinder, a pressure regulator is required. (Figure I-2b) First open the main valve; the gas pressure in the cylinder is given on the right hand gauge. Then open the regulator valve by turning the lever clockwise. Finally adjust the flow rate to the desired level by opening the needle valve. The pressure between the needle valve and the regulator is given on the left-hand gauge. The regulator will maintain the pressure. During the experiment, the flow can be halted by closing the needle valve, but when you are finished with the cylinder for the day, close the main valve to prevent loss of the gas in case the regulator leaks slightly. Do not empty a cylinder completely; leave approximately 25 psi so that the cylinder does not become contaminated with air or other gases before it is returned to the supplier for refilling.

In several experiments, N_2 gas will be used to flush air from a reaction system, as shown below. Before the reaction is begun, the N_2 flow is turned off with the stop-cock. This normally produces a pressure build-up which could result in the rupture of the tygon tubing connecting the apparatus to the nitrogen cylinder. To prevent this, it is convenient to connect an oil or mercury bubbler to the nitrogen line to act as a pressure release valve for the excess nitrogen (Figure I-3).

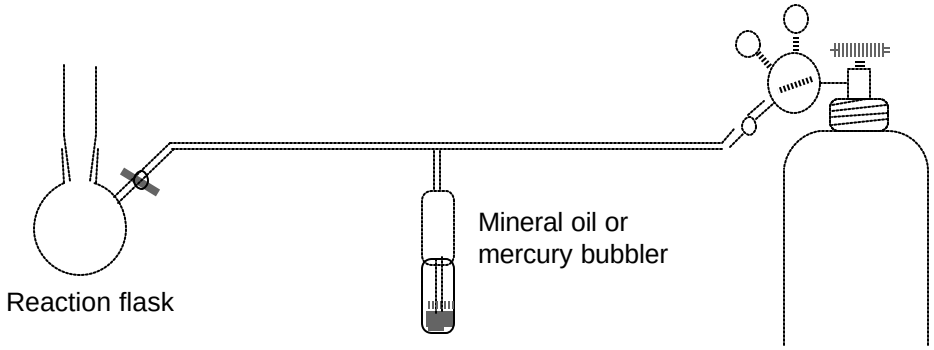


Figure I-3 In-line connection of a gas-bubbler

Handling Air-Sensitive Reagents

A large variety of air-sensitive reagents is now available commercially. Specific examples include solutions of boron complexes, organoboranes, borohydrides, Grignard reagents, organoaluminums, organolithiums, and organozincs. Since all of these reagents react with water or oxygen or both, they must never be exposed to the atmosphere.

Most modern synthetic chemists are familiar with the utility of these versatile organometallic reagents. However, because the compounds are air-sensitive or pyrophoric, some workers hesitate to make use of the remarkable chemistry of these reagents. Some chemists still believe that very specialized equipment and complicated techniques are required for handling of these materials. This is often not the case.

Air-sensitive reagents available from Aldrich Chemicals are packaged in special bottles. The Aldrich Sure/Seal packaging system (Figure I-4) provides a convenient method for storing and dispensing research quantities of air-sensitive reagents. With this bottle, reactive materials can be handled and stored without exposure to atmospheric moisture or oxygen. The reagent comes into contact only with glass and Teflon, yet it can be readily transferred using standard syringe techniques.

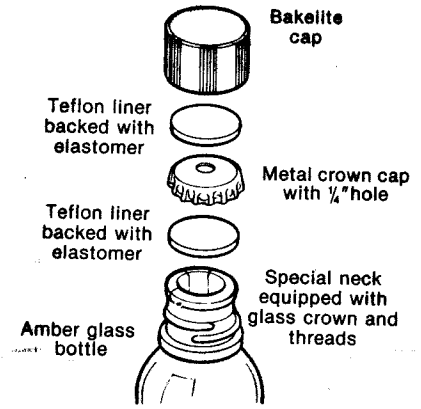

Bakelite cap
Teflon liner backed with elastomer
Metal crown cap with ¼" hole
Teflon liner backed with elastomer
Special neck equipped with glass crown and threads
Amber glass bottle

Figure I-4 The Aldrich Sure/Seal packaging system

The Bakelite cap on a Sure/Seal bottle can be removed because the crown cap, with its teflon-elastomer liner, is already crimped in place. The reagent can then be dispensed using a syringe or double-tipped needle inserted through the hole in the metal crown cap. After the needle has been withdrawn from the bottle, a small hole will remain in the Teflon/elastomer liner. Under normal circumstances, the hole in the liner will self-seal and the reagent will not deteriorate. However, the possibility exists that once an elastomer is punctured, it may leak on long-term storage. This possibility is virtually eliminated with the Sure/Seal system because when the Bakelite cap is replaced, the Teflon/elastomer liner in the cap forms a seal against the top of the metal crown. Thus, the contents are effectively protected from moisture and oxygen in the atmosphere.

Laboratory glassware contains a thin film of adsorbed moisture which can be easily removed by heating in an oven (125°C/overnight or 140°C/4 hours). The hot glassware should ideally be cooled in an inert atmosphere by assembling the glassware while still hot and the flushing with a stream of nitrogen or argon. Spring clips or rubber bands are required to secure all joints during the flushing.

Small quantities (up to 50 mL) of air-sensitive reagents may be transferred with a syringe equipped with a long needle (1-2 ft.). The long needles are used to avoid having to tip the reagent bottles. The reagent may be introduced into the reaction vessel via a rubber septum. These rubber septa slowly degrade in contact with organic vapours, and therefore will only provide a positive seal for a limited number of punctures, depending on the needle size. The lifetime of the septum may be extended by always reinserting the needle through the same hole. Ideally the syringe and plunger should be oven-dried before use. The syringe and plunger should not be assembled before being placed into the oven, and should be cooled afterwards before assembly.

The syringe transfer of liquids is readily accomplished by first pressurizing the Sure/Seal bottle with dry nitrogen, followed by filling the syringe as illustrated in Figure I-5. The nitrogen pressure is used to slowly fill the syringe with the desired volume plus a slight excess (to compensate for gas bubbles) of the reagent. Note that the nitrogen pressure pushes the plunger back as the reagent enters the syringe. The plunger should not be pulled back since this tends to cause leaks and creates gas bubbles. The excess

reagent along with any gas bubbles is forced back into the reagent bottle as shown above. The accurately measured volume of reagent in the syringe is quickly transferred to the reaction vessel by puncturing the rubber septum on the reaction flask or additional funnel, as shown below.

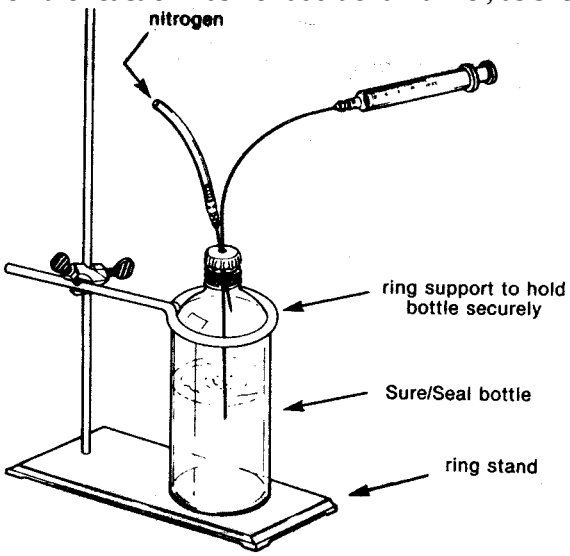


Figure I-5 Filling syringe using nitrogen pressure

When handling air-sensitive materials, it is important that the user be thoroughly familiar with the basic chemistry of the reagent. Also, the user should be prepared for unexpected problems. For example, at least one set of clean, dry syringes and needles should always be available in case the first set becomes plugged.

Measuring IR spectra using the FTIR instrument

Several of the experiments in this course require you to take an infrared spectrum of your product. These spectra record the absorbency of light by the compound in the region 4,000 to 200 cm^{-1} (wavelength 2500 to 50,000 nm.) Energies here are in the region 10-50 kJ mol^{-1}, corresponding to molecular vibrations. Only compounds with covalent bonds will absorb IR light; purely ionic crystals do not interact. So the optical 'windows' for use in IR spectroscopy are made of ionic sodium chloride, or in some special cases, CsI.

Sample preparation

Many of the spectra you will record are of solids. In some cases, IR spectra can be recorded in solution using expensive solution cells. Solids are prepared either as **mulls** (that is, a thin layer of a paste made of the solid powder dispersed with nujol or Fluorolube oil), or as KBr pellets. Nujol is a high M.W. alkane mixture, which reduces light scattering by the powder. As a saturated hydrocarbon, it has absorptions at 2820-2960 cm^{-1} (C-H stretch), 1460 cm^{-1} (CH_2 bend) and 1380 cm^{-1} (CH_3 bend). Fluorolube is a fluorinated hydrocarbon, and the C-F stretch occurs below 1400 cm^{-1}. Various deformation bands also occur in this region. The usefulness of fluorolube is in obtaining an undistorted view of the 4000-1400 cm^{-1} region. Note that mulls are not solutions!

To prepare the mull, grind a small quantity of the substance to a very fine powder, add one drop of nujol and mix to a paste. Don't use too much liquid, or you'll only see the nujol peaks! Spread a thin layer on an NaCl plate and make a 'sandwich' with a second plate. Don't have the layer too thick; if it's opaque to you, it will be opaque to the spectrometer! Insert the plate assembly into the circular sample holder, and gently screw on the top. For instructions on data collection see the next section. Follow exactly the same procedure with Fluorolube.

After use, clean the IR plates and the pestle and mortar using only the **CH_2Cl_2 provided**. (Chlorinated solvents must be used in the FUME-HOOD.) Nujol does not dissolve in water, but NaCl and especially CsI plates do, so water is NOT the solvent of choice here! Even acetone is generally too wet to use on highly polished IR plates.

KBr pressed pellets are prepared by first grinding a small quantity of IR-grade KBr powder (**hygroscopic** - stored in a desiccator! return it there!!) to a very fine powder. Then add about 5% of this quantity of solid to be analyzed and continue grinding till an intimate mixture of uniform fineness is achieved. Load the pellet press with the mixture, and apply the appropriate amount of pressure (see instructions with the hydraulic press). Carefully remove the pressed pellet with plastic tweezers and mount in the IR pellet holder for recording the data.

For solutions, use the 0.2 mm NaCl solution cell. Carefully fill with a concentrated solution of the compound in the indicated solvent. This strategy ensures that the compound peaks will not be swamped by the solvent absorptions. Note that a reference spectrum must first be recorded using the same cell containing only the pure solvent. Make sure that the cell is completely filled, with no air bubbles. **Do not let solution spill over the sides, where it will evaporate and coat the optical surface with solute**.

Collecting Data

The BOMEM EASY software package is a simple, powerful and genuinely easy-to-use program for the collection, display and plotting of FTIR data. You will use this program exclusively in the Chem 3820 lab. Normally the instrument will have been turned on ahead of time by the instructor.

> It is very important that the BOMEM FTIR be warmed up for a minimum of ONE HOUR before the sample compartment is opened. This is to prevent moisture collecting on the sensitive CsI windows which isolate the sample compartment from the sensitive optical components.

If the computer is not already on, switch it on at the main power-bar switch. When the C> prompt is displayed on the screen, type in the word: **bomem**. Then press "Enter" to start the program. From here on in, the experiment is entirely menu-driven. These menus are largely self-explanatory. For further details not discussed here, see the photocopied excerpts from the user's manual provided with the instrument.

The program now displays the Main Menu (Figure I-6a).

It is important to check that the computer has the correct directory activated. This is shown in the top right hand box, just below today's date. It should read:

c:/ftirdata/c3820

If a different subdirectory is displayed, hit function key F7 on the main menu to display the File System menu. Now hit F4 to "change directory". This will list the directories being used, and you can select the correct one with the cursor and hit "Enter" to activate it.

Take a moment to look at the files already in your directory (Figure I-6b). For **each** spectrum, there are four files. The ↓ arrow selects experiments by name. The → arrow moves into the associated right hand set, where the ↓ arrow again selects the appropriate item. A "normal" IR spectrum will be shown if the name and .TRANSMITTANCE extension are highlighted in green. Hitting "Enter" will display this experiment on the computer screen (Figure I-6c). Thus

Figure I-6 Screen images of the BOMEM EASY computer program

after recording a spectrum, you can always come back to the spectrum on screen for further analysis, without having to record it again. Note that data is **automatically** saved to disk when a spectrum is recorded. If the .RAW extension is highlighted, an odd-looking spectrum is displayed (Figure I-6d). First of all, the baseline of this spectrum is approximately bell-curved. This reflects the intensity of the light emanating from the light-source. It's maximum intensity is around 2000 cm^{-1}, and falls off in either direction from this point. As for the absorptions, this spectrum is a combination of the actual peaks in the sample (in the figure, polystyrene) and the background gases in the sample compartment of the IR instrument (mostly CO_2 and water vapour). This points out an important difference between the BOMEM and the small Perkin Elmer instruments used in the organic labs:

> *The BOMEM MB102 is a single beam instrument, and a separate background (reference) spectrum must be recorded before the sample can be measured.*

Hitting "Esc" in any menu will move you back up to the previous menu. This is called a "hierarchical menu organization." Hitting "Esc" too often will result in a prompt whether you wish to leave the program.

With nothing in the sample compartment, hit F1 on the main menu to record the Reference spectrum. You see the data acquisition menu (Figure I-6e). The title is already specified. In the Description field, you can mention something about the reference, especially if it is unusual. Hitting "Enter" moves to the other fields. Leave # of scans at ten, detector at DTGS 1mm. Sigma minimum depends on the windows you are using. For NaCl, it is 600 cm^{-1}, for KBr, 450 cm^{-1} and for CsI, 200 cm^{-1}. Leave Sigma maximum at 4000 cm^{-1}.

Now hit F1 to start acquisition.

> Never place anything on the spectrometer bench: not your coat, books, Coke and ABSOLUTELY NO CHEMICALS OF ANY KIND. Don't lean on this bench, nor let anyone else do so. Jarring the spectrometer during data collection will result in a poor spectrum.

After collecting 10 interferograms, the computer averages the data and performs a fast Fourier transform, which is displayed on the screen. You should see something similar to the "RAW" spectrum (Figure I-6d). Hit "Esc" to return to main menu. Now hit F2 to record a transmittance spectrum (the only kind we will do in this course).

The data acquisition screen will now allow you to fill in the name of the experiment in the first field (Figure I-6f). Please start all experiment names with your own name, followed by the compound type, e.g. if Sally Johnson is collecting data for the siloxane trimmer of Experiment 2, she might enter:

SJEX2#1

This will prevent confusion between the same compounds from each student. Keep the file name as short as possible! In the description field, you can add some explanatory notes to distinguish this sample from any others, e.g.:

Siloxane trimmer in CS2 solution - NaCl cells

Now press F1 to start acquisition.

Displaying and plotting spectrum

After ten scans and transformation, your spectrum will be displayed on a screen as in Figure I-6c. You should learn certain commands which allow you to view specific regions of the trace, or expand a region of interest. In particular, the following:

- A vertical and horizontal cursor are displayed. These can be manipulated with the arrow keys.
- Pressing an arrow key while holding down the "Alt" key zooms the curve in the sense indicated by direction, with the zooming action centered about the current position of the cursor.
- Pressing an arrow key while holding down the "Shift" key moves the whole spectrum in the indicated direction.
- "Home" resets cursors to middle.
- "Home" + "Shift" resets horizontal zoom.
- "Home" + "Alt" resets vertical zoom.
- "Page Up" and "Page Down" switch between displayed spectra in multiple curve mode.

The function keys at the bottom are used for the purposes indicated.

- F4-Analysis is used to mark the more intense peaks so that a numerical list of peaks vs. intensity can be printed out. Follow directions in the resulting menu.
- F7-Multiple curves is used to switch between various modes of display when more than one spectrum is in memory at once. This can be very useful in comparing a known spectrum to an unknown, or for looking for small differences between spectra of quite similar compounds.
- F1-Hardcopy is used to obtain a printout. To use the digital plotter for output, consult your instructor on the correct method for loading the plotter with paper. Within the "hardcopy" menu, F1 - F4 refer to different plotting options. However, it is usually more useful to plot from within the "analysis" menu, where F6 provides a "full-description" plot on the digital plotter, with the highlighted peaks labeled with the peak-positions in wavenumbers.

- An alternative is to use the dot-matrix printer for output. Then your only option is F6-Print Screen. Then go back to the previous menu and select F4 and subsequently adjust the tolerance level till only the 20 or so most prominent peaks are displayed with red markers. Then press F4 to get a printout of these peak positions (i.e. the ones which were marked.)

NOTE: the paper can be rolled back in the printer BEFORE the numerical peak dump is activated to save wasting a blank sheet of paper. The printer does this automatically by (i) pressing the Function keypad, followed by (ii) the On Line keypad. The paper rolls back to exactly the right position and the printer automatically is ready to print again. Unless your peak list goes right to the bottom of the paper, just tear off the page after printing, so as to leave the printer ready for the next user with the paper in the right position.

Obtaining solution spectra on the BOMEM single-beam FTIR

The procedure to be used with the BOMEM Easy software for collecting solution spectra is a little different from that described above. First, locate the solid NaCl cavity cells (Figure I-7). A small plastic cap is provided to seal the cell after filling. The cross-section of the 0.2 mm cell is shown in Figure I-7b. The larger regions along the sides allow for filling with a small syringe needle. Take care not to damage the crystal in the narrow region.

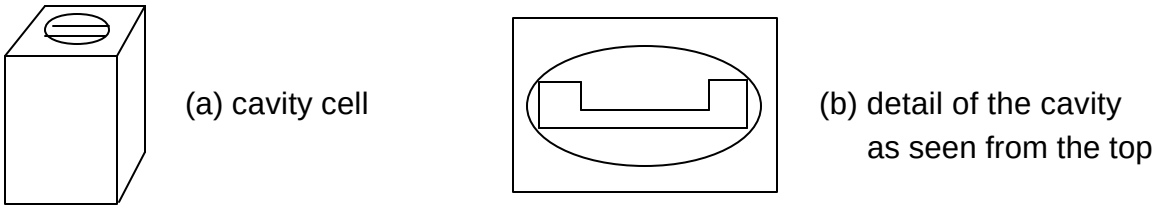


Figure I-7 The NaCl solid cavity cell for solution IR spectra

Fill the cell with pure solvent

Using the syringe, fill the cell with pure solvent identical to that to be used for the solution spectrum. Guidance in choosing the solvent is provided in the lecture material, or can be obtained from the book entitled "The chemist's companion". Ensure that there are no air bubbles trapped in the narrow region of the cell, where the data will be collected. If necessary, tap the cell gently on a desk to drive away any bubbles.

Collect a transmittance spectrum of solvent

Collect as "Reference" an empty spectrometer compartment. Then insert the cell filled with pure solvent (Capped!) into the cell-holder and mount on the optical bench. Collect a transmittance spectrum, and call it "solvent".

Collect a transmittance spectrum of the solution

Prepare a relatively concentrated solution of the compound to be analyzed in the chosen solvent. Empty the solvent out of the cell by shaking it out in a fume hood. Fill the cell once with the solution, using the syringe. Shake it empty once more, and fill again. Cap the cell and mount it in the holder on the optical bench. Collect the transmittance spectrum, call it "solution".

Subtraction of the spectra

Hit ESC to get to the main menu. Use F5 Display to call up SOLUTION.RAW, the **raw** spectrum for the solution. This includes the background due to air. Now use F2 Manipulate Graph and again F2 Spectral subtraction. Call up SOLVENT.RAW, and use F1 to adjust the mix factor with the arrow keys until the baseline is smooth. When you are satisfied, hit ESC, whereupon the system prompts you (in green letters) for a description of the new file, which will be saved as SOLUTION.SUBTRACTION. Analyze and plot this new spectrum in the usual manner.

The procedure outlined here is necessary, since the automatic algorithm for subtracting reference from sample spectra cannot handle the intense absorptions of the solvent peaks.

Obtaining a KBr disc spectrum

Introduction

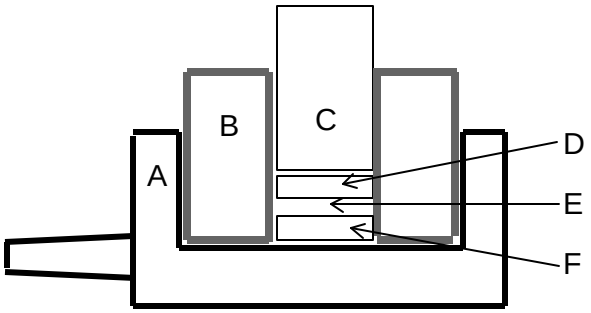
Potassium bromide powder can be pressed at about 10 tons pressure into clear discs having high transmission throughout the 4000 to 450 cm-1 range of the infrared instrument. Before pressing, samples may be mixed with the KBr powder at a sample concentration level of 0.1% to 2%, and their spectra obtained in the KBr matrix. As in the mulling technique, the sample must be very finely ground in order to reduce scattering losses and absorption band distortions.

A word of caution concerning the KBr technique is required. Modifications in the spectra of some samples may occur due to ion exchange with the KBr matrix, pressure effects, or transformations to other crystalline forms. This does not detract from the general usefulness of the technique, but must be kept in mind when comparing unknown spectra obtained as KBr discs with known or standard spectra obtained by other techniques.

Preparation of the blank KBr disc

Place the body of the die on its base. (Consult Figure I-8 for the die parts referred to in this discussion.) Insert the small, lower polished disk F into the die opening with the shiny surface up (i.e. into the bottom of B). Firmly but gently insert B into A, and set upright on the bench top. Using the weighing paper as a funnel, completely transfer 0.30 g (weighed on a top-loader balance) of infrared quality KBr powder to the die opening. (Use KBr that has been oven-dried and cooled and stored in a desiccator.)

Insert the upper polished disk D face down, followed by the plunger C (beveled edge up), and with a light rotary motion of the plunger, level the sample. Carry the whole assembly, as well as (i) clear plastic ring (ii) plastic forceps (iii) spring-loaded disc-holder to the small grey press located next to the machine-shop on level 8. Connect the die to the vacuum pump via the rubber hose provided, and evacuate the die to a pressure of 1 to 2 mm of Hg for about 2 minutes to remove air from between the KBr particles.



A - Body of die, with vacuum nozzle

B - Inner part of die

C - Die plunger

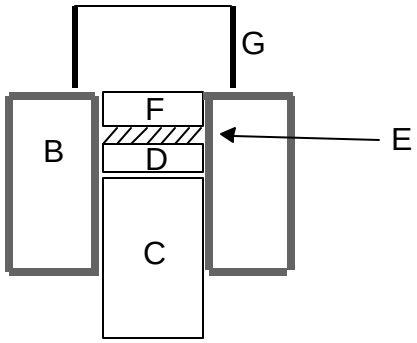
D - Upper polished disk, face down

E - KBr plus sample

F - Lower polished disk, face up

Figure I-8

With the vacuum still connected, place the die on press. There should be two 5cm thick round spacers on the piston head, leaving just enough space to place the die assembly below the top platen. The needle valve at the left-hand-side of the press should be gently pulled up towards you to close the hydraulic valve before pressing. Press for 3-4 minutes at **9 tons pressure on the middle scale of the press dial**. This actually delivers a total pressure of 30 tons on the 13mm die. Disconnect the die from the vacuum line, relieve the pressure on the press by lowering the needle valve handle away from you, and remove the die.



B - Inner part of die

C - Die plunger

D - Upper polished disk, face down

E - KBr finnished pellet

F - Lower polished disk, face up

G - Clear plastic ring

Figure I-9 Set-up for the removal of the disc

Invert the die and remove base A. Place the inverted die back in the press and center the clear plastic ring on the die so that the lower plunger will be visible when forced from the die, as in Figure I-9. Now, with the press, force the plunger upward until the lower ram and disc just clear the body of the die. Remove the die from the press, and with the tweezers, place the disc, which should be homogeneous in appearance and transparent, in the disc holder. Insert the disc holder in the instrument and obtain the spectrum in the usual manner.

The spectrum should resemble that shown in Figure I-8.

Figure I-10 IR spectrum of a blank KBr disk

Grinding of samples and preparation of a KBr disc.

Place an estimated 10 to 15 mg of the sample in the agate mortar. Grind the sample with a vigorous, firm, rotary motion, restricting the sample as much as possible to about ¼ to ½ of the mortar. Scrape the ground sample from the sides of the mortar with the micro spatula and discard all but about 1 mg. Weigh 0.30 g of dry KBr powder as before, and add 5 to 10 mg to the mortar containing the sample. Use the pestle to mix the KBr and sample with a gentle rubbing motion. Do not grind the KBr during the mixing procedure since reduction

in particle size is not required and will lead to adsorption of water on the KBr. Now add 15 mg of KBr powder and mix as before. Add another amount of KBr approximately equal to the total quantity in the mortar (i.e., add about 30 mg) and mix. Continue adding and mixing KBr in this manner until all the KBr is in the mortar. If this procedure is followed, a homogeneous mixture of the sample and KBr, with little H_2O pickup on the KBr, will result. Completely transfer the mixture from the mortar to the die using the weighing paper and press the disc as described above. Remove the disc from the die, mount it in the KBr disc holder, and obtain the spectrum.

Chemistry Laboratory Rules and Safety Precautions

1. Never work alone in the laboratory.

2. Smoking and eating are not permitted.

3. Unauthorized experiments are prohibited.

4. Know the location and use of the fire extinguisher, safety showers and first aid kit.

5. It is required that you wear **prescription glasses** or **safety glasses** at all times in the laboratory for your own protection. Contact lenses are particularly dangerous and they **must not be worn** in the laboratory.

6. Report all injuries to your instructor at once.

7. Never taste chemicals or solutions.

8. Use the fume hoods at the sides of the laboratory for all poisonous reactions or any reactions which produce noxious gases.

9. When diluting concentrated acid or base always add the concentrated acid or base to water (never the reverse), while stirring the solution. Be very careful with sulfuric acid.

10. Keep an orderly, clean laboratory desk. Return glassware to the lab drawer when finished using it to keep the work area from becoming cluttered.

11. Leave unneeded books, etc. outside of the laboratory. Never block aisles with personal effects, or leave clothing, etc. on the benches.

12. Waste crocks are provided for the disposal of all solid chemicals and paper, etc.
    (1) Non-chlorinated solvents
    (2) Chlorinated solvents
    (3) Sulfur chlorides

14. Stock reagent bottles are placed on the side bench or beside the balances; leave them at that position.

15. Always read the label twice before taking any chemical from a bottle. If you are not sure if you have the right chemical, ask!

16. When pouring reagents, hold the bottle so the label points upwards facing the palm of the hand. The accumulation of reagent on bottle lip may be removed by touching the bottle lip to the rim of the receiving vessel.

17. Avoid using an excess of reagent. If you happen to have measured out too much, see if someone else can use the excess.

18. Due to possible contamination of the contents of a whole stock bottle, never return unused chemical to the stock bottle.

19. Always check your glassware before you use it. If it is broken or cracked, exchange it for a new one.

20. There is one crock reserved for broken glass. All broken glassware should be placed in this crock and no other.

21. If corrosive chemicals or liquids come in contact with the skin or clothing, flood with copious amounts of water for an extended period of time.

22. Spilled chemicals should be wiped up immediately; spilled acid or base should be rinsed with plenty of water and wiped up with a sponge and the sponge rinsed after.

23. Inserting glass tubing or thermometers through a rubber stopper - first lubricate the tube and stopper with glycerol or water, then holding the tube near the end to be inserted insert slowly while rotating the tube. BE VERY CAREFUL!

24. When you are ready to leave the laboratory, your bench area should be rinsed off with a wet sponge and the water, gas, and air valves shut off.

25. The chemistry store room is out of bounds to students. If you require apparatus, ask your instructor for it.

26. Disposable polyethylene gloves are provided; other glove materials may not protect you against the chemicals handled in this lab

Consent Form

This form must be completed, signed, and submitted to the laboratory instructor before any laboratory work is begun.

* * * * * * * *

I have read and understood the safety rules that appear on pages I-33 and I-34 of this manual, recognize that it is my responsibility to observe them, and agree to abide by them throughout this course.

Name (please print) _____

Date _____ Signature _____

Glassblowing course

Fundamental Glass Manipulation

Cutting glass

There are a number of ways in which glass tubing can be cut but some techniques are better than others. The method preferred is by flame cutting which is carried out in the following manner. Rotate the tube to be cut in the flame and when the glass reaches the working temperature, pull it apart. (Fig. I-11A) Redirect the flame to the front of the shoulder and pull off the existing "point" (Fig. I-11B). Reheat the end of the tubing again and blow it out (Fig. I-11C). With a piece of glass rod carefully chip off the feather edge and apply heat to the end of the tube until the wall thickness is uniform. With this method, the possibility of pinhole leaks when making a join is reduced and the seal can be worked to that it is invisible.

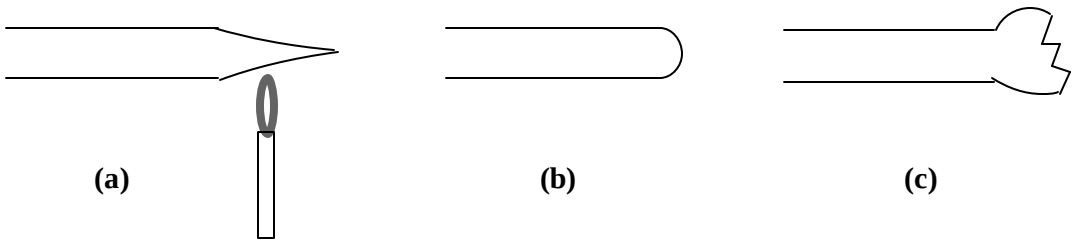


Figure I-11

The most common method of cutting tubing however, is the scratch technique. This is accomplished by placing a scratch with a glass knife perpendicular to the tube axis, and with the scratch facing up, apply downward pressure at the end of the tubing with the forearm and pulling up and outward with the thumb at the scratch. Fig. I-12 illustrates.

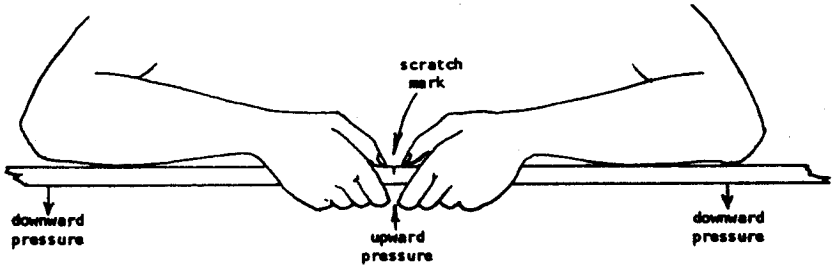


Figure I-12

In addition to the foregoing method, cracking or cutting of large tubing can be made easier if a piece of glass rod is heated to the melting point and is placed on the middle of the scratch previously made on the tube. Fig. I-13 illustrates.

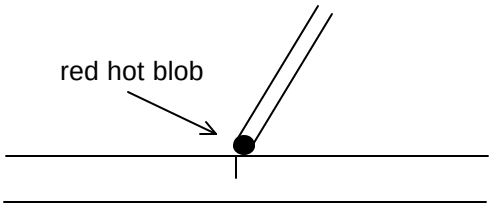


Figure I-13

Quite often a situation arises where a short section of glass tubing has to be removed. This can be a difficult task using the methods described. A simple method to accomplish this is as follows. Make a fairly long deep scratch perpendicular across the tube to be cut and with the scratch facing up, apply an intense needle flame at the end of the scratch furthest away from you. The tube will fracture along the scratch and the short section can then be removed with the aid of tweezers. Fig. I-14 illustrates.

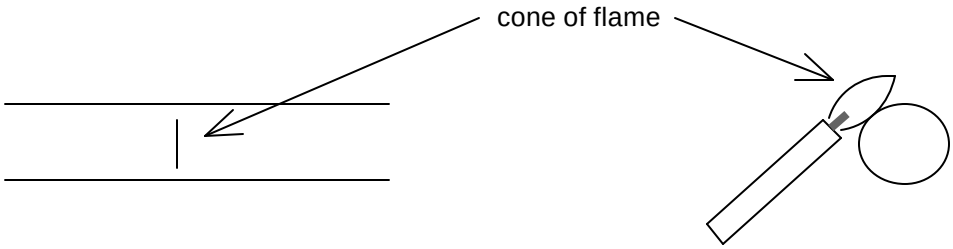


Figure I-14

Another cutting method which is ordinarily available in a professional shop only is a glass cutting saw.

Hand Working Technique

A glassblowing operation is done with the apparatus corked up; a blow hose is useful. The effects brought about by positive pressure in a closed system is expansion at the softened area; negative pressure will cause collapse. By varying the pressure, a piece of glass tubing can be given an entirely different shape simply by blowing or sucking on the blow hose while the glass is soft.

By applying heat to a piece of tubing and merely pulling on it, several things happen; the tube length is increased and the wall thickness becomes thin. Similarly, if the tubing is heated and the ends are pushed together, then the wall will be thickened and the overall length of the tube will be shortened.

When a piece of glass is heated to the working point, gravitational force will cause it to flow downward. For this reason, rotation of the glass while it is being worked is necessary.

Since the surface tension of glass is relatively high, glass protrusions when heated will tend to flow in causing the glass to become thick at that point.

As with most other compounds, superheating can cause changes in certain properties of glass. When these changes occur, the glass becomes cloudy in appearance and loses its flow properties when reheated to the working point.

When glass is cooled from the softening point, it goes through a crystallizing temperature range. If the glass is twisted or flexed in any way at these temperatures, it will become translucent and appear crystalline. This devitrification can be cured by reheating the glass to the working point.

Pulling A Point On Glass Tubing

There are many fundamental procedures with which a glass worker has to become familiar, but most involve the ability to rotate two pieces of glass tubing synchronously. Because this is quite difficult to master, a simple method called "Point Pulling" was devised. The following procedure illustrates this method.

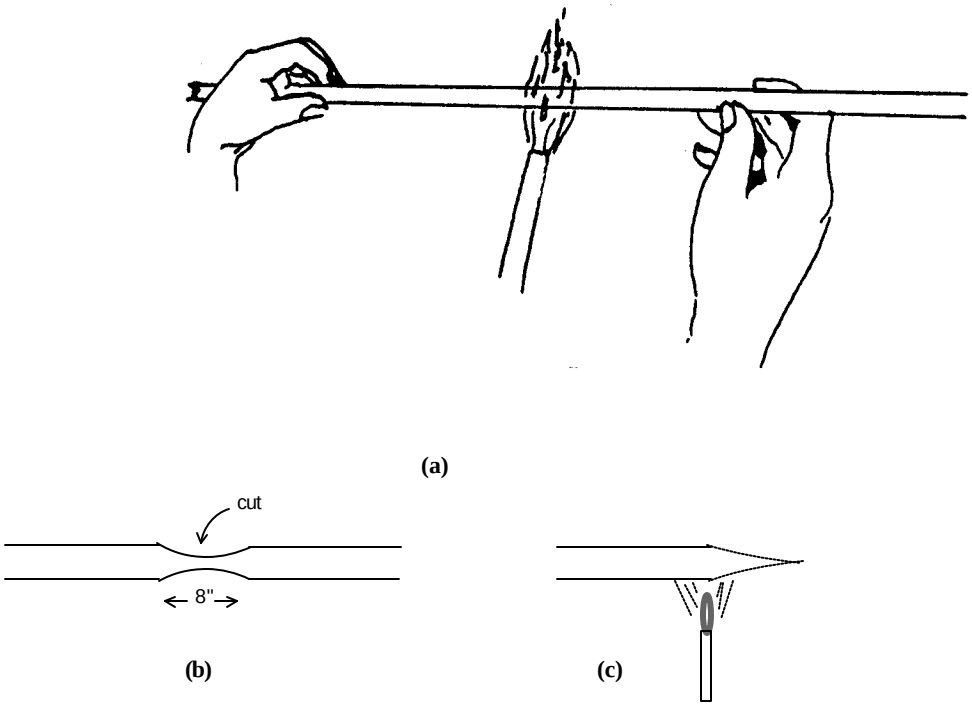


Figure I-15

A piece of tubing 12 or 13 mm diameter, approximately 60 cm long, is cleaned and dried. The tube is then held in the hands as illustrated in Fig. I-15a. A soft bushy flame is directed to the midpoint of the tubing as it is being rotated. When the heated glass begins to soften the ends of the tube are pushed

together slightly over a period of time until the softened glass area becomes thick. The tube is then removed from the flame and the ends slowly pulled apart until the diameter at the midpoint is about 5 mm. When cool, the tubing is scratched with a knife at the narrowest point and separated into two pieces (Fig. I-15b)
The synchronous rotation of the tubing when in the softened state is of the utmost importance for two reasons:

(a) To attain uniformity of temperature around the entire periphery.
(b) To prevent twisting and/or buckling of the glass.

Now, take one of the pieces and hold it so that the right hand supports the point only and the flame is directed just back from the shoulder of the tubing. Fig. I-15c. This operation of Point Pulling is repeated until the point, when rotated in the fingers, is aligned with the axis of the tubing.

Constricting a Glass Tube

Illustrated in Fig. I-16 are two common types of constrictions. The method for fabricating these is as follows: hold and rotate the tubing in the usual manner and direct a bushy flame at a segment of it. If a constriction similar to Fig. I-12a is required, push on the tube ends to gather glass and thicken it at the point where it is heated. If a constriction similar to Fig. I-12b is desired, as a final step, pull on the tube ends slightly over a period of time until the desired internal diameter is achieved.

(a) **(b)**

Figure I-16

Assigned glassblowing projects

1. Joining Glass Tubing of the Same Diameter

Cut two pieces of 8 mm O.D. tubing to be 10 cm and 20 cm in length and cork one end of the 20 cm piece. Hold both pieces in the fingers as illustrated in Fig. I-15a. (The tubing must be held in this manner to allow the worker to blow into the end of the short piece and rotate the tubing simultaneously.) As the tubing is rotated, direct a soft bushy flame to the tube ends (Figure I-17a). When the glass begins to flow push the tubes together, then pull slightly in an attempt to thin the glass at the butt. Fig. I-17b. The join is then reheated and expanded by blowing into the open end of the tube. Fig. I-17c. The glass butt in reheated once again until the expanded section is reduced to the same diameter as the tubing. Fig. I-17d.

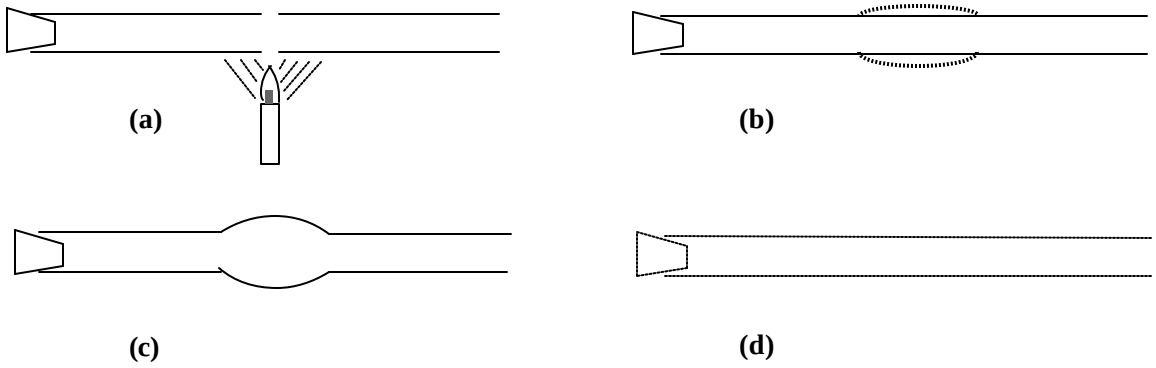


Figure I-17

2. Joining Glass Tubing of Different Diameters

Before tubing of different diameters can be joined, one end of the larger diameter must be modified as follows. Connect a blowhose assembly to one end of the larger diameter tube (20mm) and rotate it with the left hand. Direct the flame to the other end of the tube as shown. Fig. I-18a. When the glass flows, with the aid of a pair of tweezers or glass rod, pull off the end as illustrated. Fig. I-18b. After the test tube end is accomplished (Fig. I-18c) reheat it and blow a hole of approximately the same diameter as the smaller tube (8mm). Fig. I-18d, I-18e.

Cork one end of the tubing to be joined, then heat both ends as illustrated. Fig. I-18e. (A greater portion of the flame should be directed to the larger diameter tube since more heat is required to soften it than to soften the smaller diameter tube.) When the ends begin to flow, join them and blow slightly. Fig. I-18f. Reheat the junction, expand the thickened glass by blowing, then pull the ends slightly. Fig. I-18g.

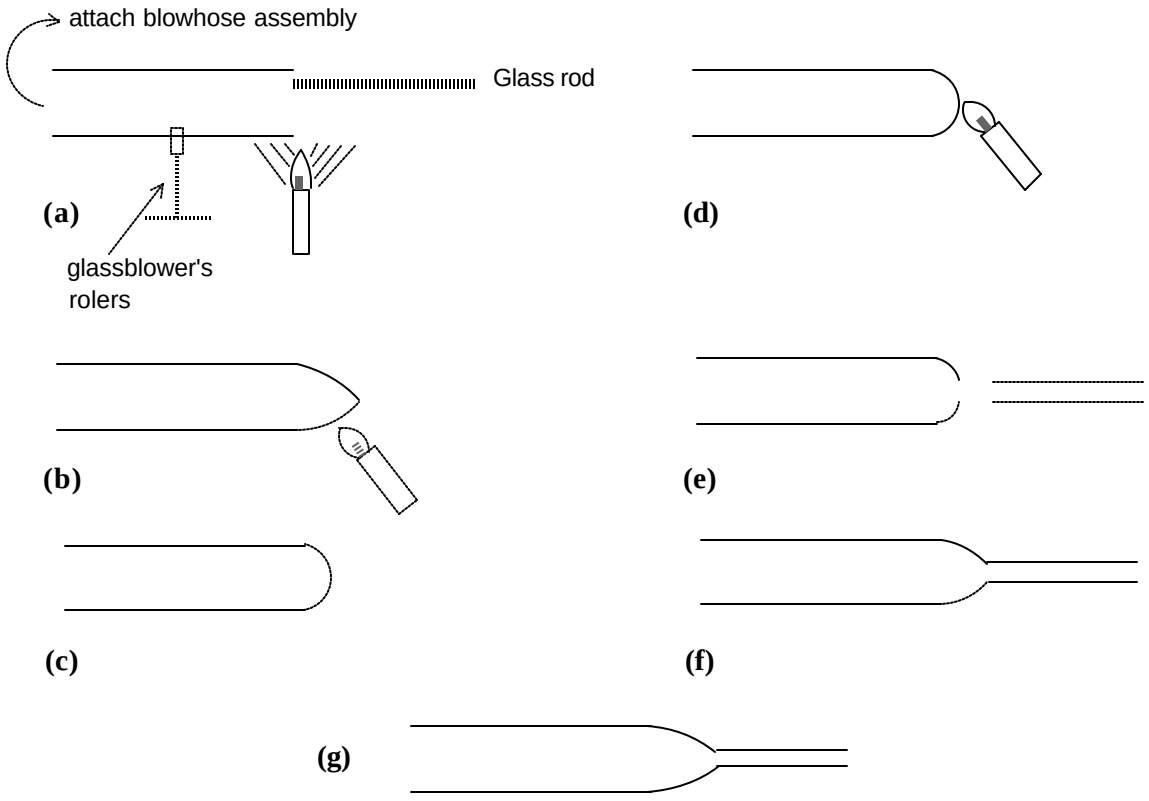


Figure I-18

3. Making T Pieces

From tubing 8 mm O.D. cut two pieces 150 cm and 80 cm in length. Cork one end of both tubes and fit a blowhose assembly over the open end of the longer piece. Direct a small needle flame to a spot near the midpoint of this tube. Do not rotate the tube. When the glass reaches the working temperature remove it from the flame and blow slightly. A slight bulge will appear. Fig. I-19a.

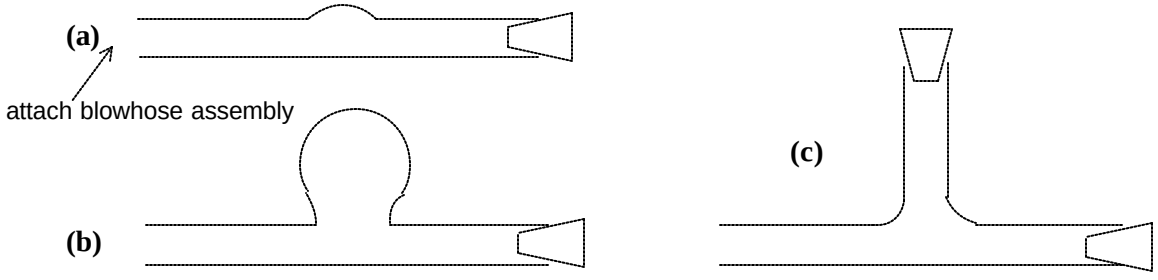


Figure I-19

Reheat the bulge until it collapses then quickly remove the tube from the flame and blow into the assembly until the wall ruptures. Fig. I-19b. (The hole should not be larger than the diameter of the side arm to be joined.) After removing excess glass fragmentation with a piece of glass rod, direct a flame around the opening in an attempt to trim the uneven thin wall.

With the right hand position the short piece of glass tubing as shown in Fig. I-19c. Heat both openings, join the tubes together, then check "T" alignment. (If a small gap in the join should result due to improper positioning, take a piece of glass rod and heat it and the gap
simultaneously to the flow point and knit the pieces together. After the gap is closed, remove the excess glass by reheating the area, dabbing the glass rod on the thickened part and pulling it away.)

Work the glass at the join by spot heating and blowing. This method ensures that rigidity of the "T" is maintained. (It is important that the entire area be kept reasonably warm while the join is being worked, as severe thermal shock could cause the "strained" glass to fracture.) Anneal the glass immediately after the "T" piece is completed.

4. Bending Tubing at Right Angles

Bending small diameter tubing is relatively simple providing the worker follows this procedure. Cork one end of a piece of 8 mm O.D. tubing approximately 20 cm long and heat it in a wide bushy flame. Rotate the tubing in the usual manner, but in addition, move it from side to side in the flame while it is being rotated to heat a greater length along the tube. When the tubing reaches the working point, quickly remove it from the flame (stop rotating), bend the open end up toward the mouth and blow. Check the bend for alignment, etc. (Figure I-20).

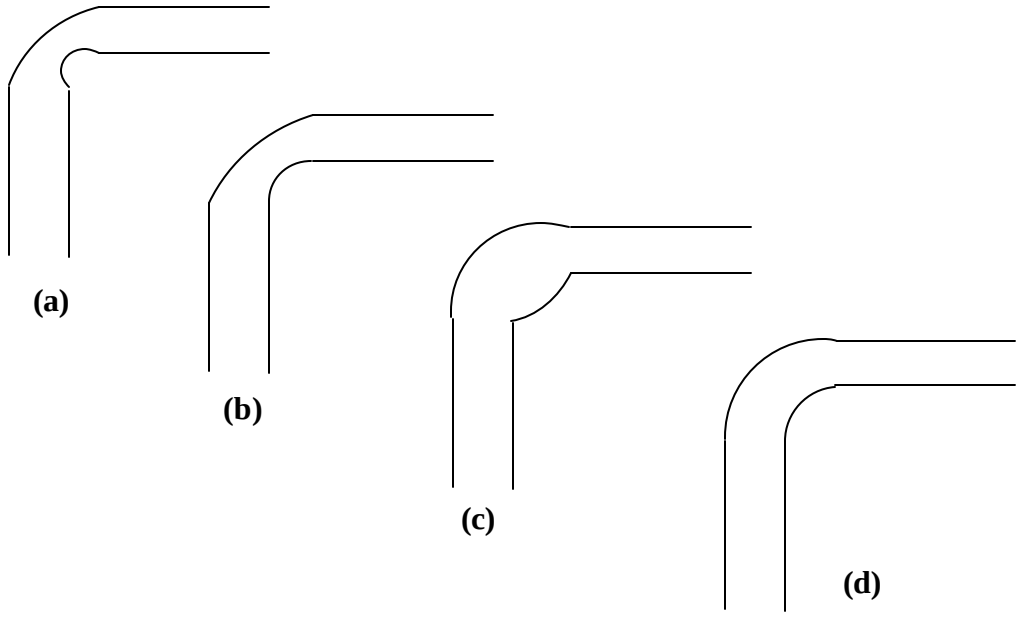


Figure I-20

(a) Bend is too sharp causing it to kink; a longer section of tubing should have been heated

(b) More air pressure should have been applied

(c) Too much air pressure was applied

(d) Satisfactory bend

5. Putting a side-arm on a test-tube (Schlenk tube)

Take a 20 cm length of 20 mm tubing, and heat the end to make a test-tube end (see Figure I-18a-d). Near the mid-point of the tubing, heat it in a low flame over a wide area around the attachment point. Then make a narrow flame, and heat the attachment point to red heat (Figure I-21a). Blow out a small hole in the larger tube equal to the size of the side-arm to be attached (8mm) (Figure I-21b). Reheat this bulge, and blow out a large bubble. Remove the devitrified glass from the hole (Figure I-21c). Attach the 8mm tubing, which should be at least 10cm long and be corked or sealed at the end, to the larger tube as follows. Heat both pieces to red heat and carefully join them at one point (figure I-21d). Then bend the tube in until it is attached at all points in the circumference.

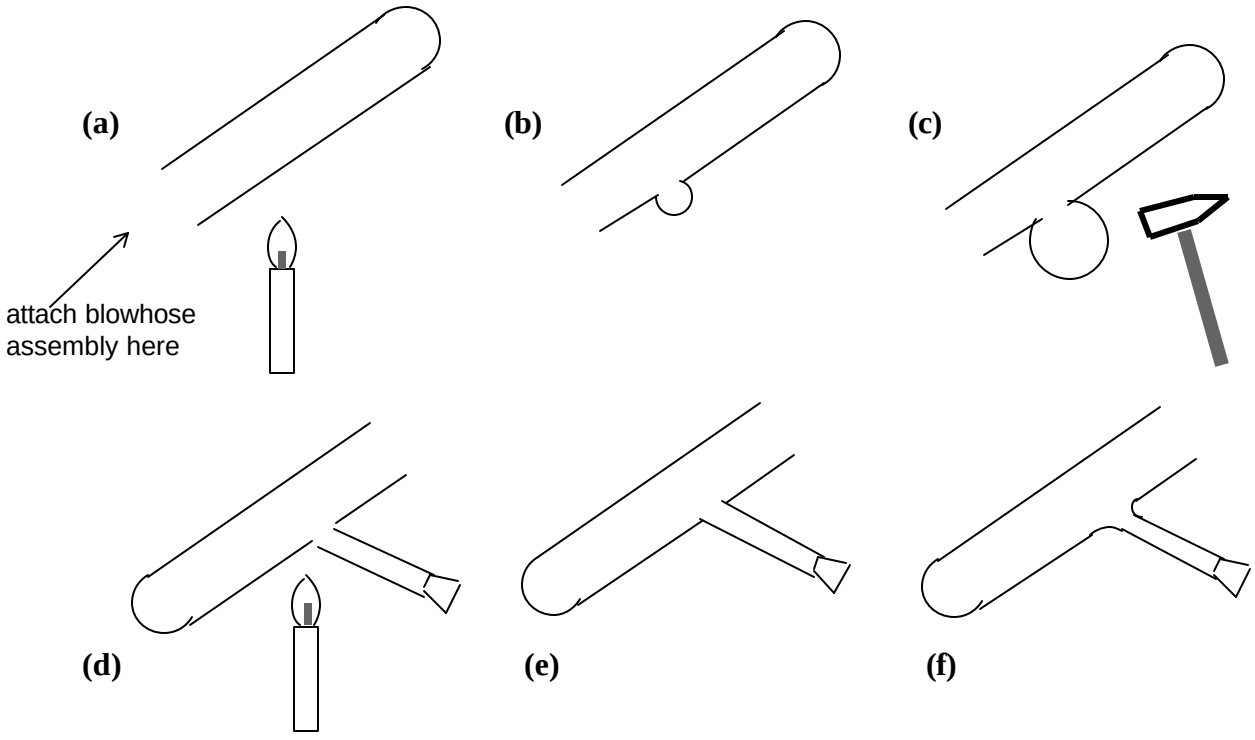


Figure I-21

Use gentle blowing to enlarge the size of the attachment point, with the goal of achieving a uniform thickness from the walls of the larger tube to the walls of the tube. The excess glass which has accumulated in the joining process is converted into increased diameter of the hole (Figure I-21e & f).

When a reasonable join is obtained, carefully and thoroughly anneal the join in a cool flame. After annealing and cooling, the side-arm can be cut about 2 cm from the larger tube, and the cut end is flame-polished to remove sharp edges. Finally the open end of the larger tube is cut back to 3-4 cm above the attachement point and also flame-polished.

Evaluation

Bring the completed projects to your instructor, who will evaluate them according to functionality and, to a lesser extent, appearance. At least three of your projects must be judged "satisfactory" to pass the lab course. All glassblowing projects must be submitted no more than **two weeks** after the end of your assigned sessions.